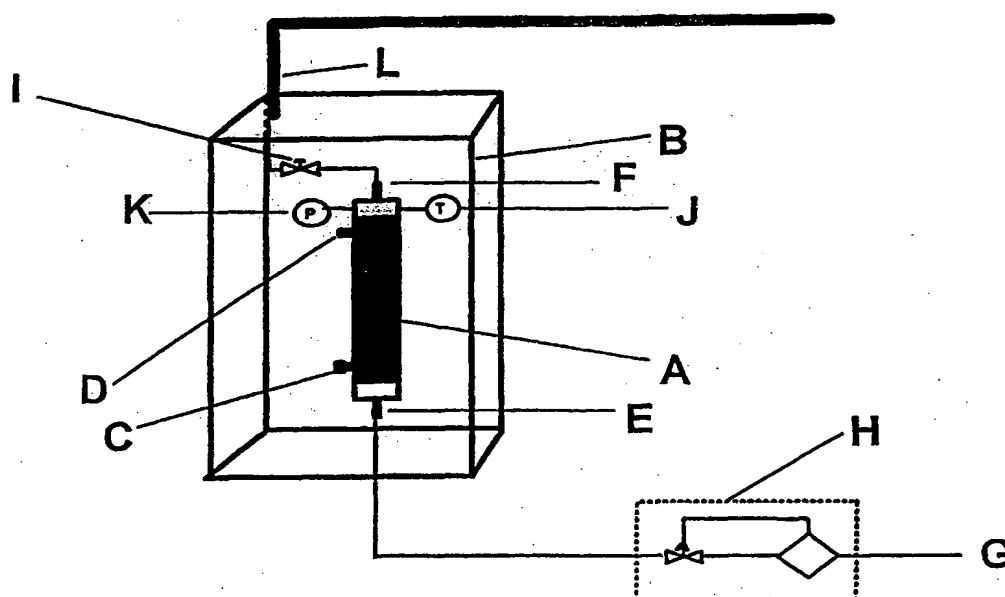




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<b>(21) International Application Number:</b> PCT/DK99/00479 <b>(22) International Filing Date:</b> 10 September 1999 (10.09.99) <b>(30) Priority Data:</b> PA 1998 01145 10 September 1998 (10.09.98) DK <b>(71) Applicant (for all designated States except US):</b> FLS MILJØ A/S [DK/DK]; Ramsingsvej 30, DK-2500 Valby (DK). <b>(72) Inventor; and</b> <b>(75) Inventor/Applicant (for US only):</b> IVERSEN, Steen, Brummerstedt [DK/DK]; Gøngehusvej 117, DK-2950 Vedbæk (DK). <b>(74) Agent:</b> PLOUGMANN, VINGTOFT & PARTNERS A/S; Sankt Annæ Plads 11, P.O. Box 3007, DK-1021 Copenhagen K (DK).		<b>(81) Designated States:</b> AE, AL, AM, AT, AT (Utility model), AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CR, CU, CZ, CZ (Utility model), DE, DE (Utility model), DK, DK (Utility model), EE, EE (Utility model), ES, FI, FI (Utility model), GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SK (Utility model), SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).  <b>Published</b> <i>With international search report.</i>

**(54) Title:** METHOD AND APPARATUS FOR PRODUCING A GAS HAVING A CONTROLLED RELEASE

**(57) Abstract**

The present invention relates to a method and apparatus for producing a gas having a controlled content of one or more species, i.e. the controlled mass transfer of one or more substances between a first fluid and a current of a second fluid, the second fluid being a gas phase. More specifically, the invention relates to a method for controlled mass transfer of one or more gas species from a first fluid to a second fluid.

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# METHOD AND APPARATUS FOR PRODUCING A GAS HAVING A CONTROLLED RELEASE

## 5 FIELD OF INVENTION

This invention relates to a method and apparatus for producing a gas having a controlled content of one or more species, i.e. the controlled mass transfer of one or more substances between a first fluid and a current of a second  
10 fluid, the second fluid being a gas phase. More specifically, the invention relates to a method for controlled mass transfer of one or more gas species from a first fluid to a second fluid in which

- the first fluid is contacted with the outer surface of a  
15 plurality of tubular members, at least part, but preferable all, of the walls of the hollow tubular members comprising a semipermeable membrane, and contacting the second fluid with the inner surface of said hollow tubular members, the hollow tubular members being arranged parallel to each other or at  
20 angles to each other, the plurality of hollow tubular members defining a membrane array, said membrane array being potted into a common housing in order to seal the inner surface from the outer membrane surface, the housing comprising connections for inlet and outlet flow of said  
25 second fluid and at least one manifold for addition of said first fluid,
- said membrane array is used in an assembly comprising means for measuring the liquid temperature, liquid pressure and optionally the liquid composition,
- 30 -said assembly further comprising a controllable heat supply.

## BACKGROUND OF INVENTION

35 It is becoming increasingly necessary to accurately measure gas compositions in process streams and in particular to measure stack gas emissions. It is essential that the

measurement system is capable of producing quick and reliable results when operated in a harsh environment by semiskilled technicians. Reliability and availability is of particular importance in an environment where down time is expensive (H.H. Willard, Instrumental Methods of Analysis, 7. ed., Wadsworth Publishing Company, 790, 1988).

A number of systems exists for measurement of compositions of gas streams. The systems can be divided into continuous and discrete techniques. Continuous systems are usually required for process control and emission monitoring. Continuous measurements of gas compositions may be performed in situ or by extractive systems. Both systems have several drawbacks.

In situ analyzers have a fast response, which makes them suitable for process control. Such analyzers are, however, difficult to calibrate or requires large amount of expensive calibration gas. Hence, extractive systems are commonly used for emission monitoring.

In extractive systems a gas sample is withdrawn from the main gas stream, typically through a probe comprising filters for removal of particulates. Subsequently the gas sample is transported to the analyzers in a sample line. The analytical system may contain means for further gas conditioning prior to the analyzers (A.G. Clarke, "Industrial Air Pollution Control Monitoring", Chapman and Hall)

The analytical system may comprise a wide range of measurement principles such as paramagnetic, chemiluminescent emission, ultraviolet or infrared absorption depending of the specific species to be measured. Multi component analyzers such as process mass spectrometers, Fourier Transformed InfraRed (FTIR)

analyzers and laser based emission monitors are also becoming available.

- 5 For accurate measurements such analytical systems must be frequently calibrated leading to reduced availability, increased service time and consumption of expensive calibration gases.
- 10 In most cases of emission monitoring, the sample to be measured contains water vapor. Combustion gases, for example, may contain as much as 15 % water vapor by volume. The presence of water vapor in a gas sample may significantly be a source of error affecting the
- 15 measurement of emissions for most measurement principles. If an chemiluminescence analyzer is used to measure nitric oxide in such a gas, water vapor will negatively affect the operation of the analyzer and, a wet exhaust gas, for example, may contain as much as 15 % water vapor, the
- 20 indicated amount of NO may be as much as 30 % below the actual present in the sample (US 4,385,910). In contrast, water vapor in the exhaust gas will positively influence the analysis mechanism in an uncompensated infrared analyzer resulting in an indicated NO measurement higher than the
- 25 amount of present in the sample (US 4,385,910). Other analytical principles such as paramagnetic oxygen analyzers require a dry sample gas for measurements.

Hence, the presence of water may introduce cross

30 interference's. A number of attempts have been made in response to the above problems.

One technique is to remove water in a gas dryer in a conditioning step prior to the analyzers, and perform a dry

35 measurement. This technique is relatively inexpensive but has the disadvantage that residual water may cause significant levels of cross interference in particular when

low concentrations have to be measured. Gases containing water soluble gases such as hydrochloric acid, HCl, nitrogen dioxide (NO<sub>2</sub>), sulfur oxides (SO<sub>3</sub>, SO<sub>2</sub>) etc. may also be fully or partly lost in the drying step. The composition of the resultant gas is thereby undesirably altered. The amount of loss varies with the flow rate and saturation level of the gas (J. Turnbull, "CEM's - Sample Handling and Calibration", In proceedings for CEM98, International Conference on Emission Monitoring, Teddington, UK, April 22.-24., 1998, p. 184-192). Further, analyzers are typically calibrated using certified dry calibration gases with nitrogen or argon as balance gas. The absence of water in these gases may significantly change system response time due to changes in adsorption equilibria (see example 2). Thus leading to higher calibration gas consumptions and reduced availability.

Another technique is to measure the wet gas at high temperature and correcting for the water content. In order to obtain an accurate direct measurement an accurate continuous measurement of the water concentration is required. Obviously, this method is more expensive and requires controlled humidification of the certified calibration gases to establish correction factors and for calibration of the water analyzer (J. Turnbull, "CEM's - Sample Handling and Calibration", In proceedings for CEM98, International Conference on Emission Monitoring, Teddington, UK, April 22.-24., 1998, p. 184-192).

Unfortunately, calibrations standards are not available for concentrations of water and generating calibration samples is considered to be notoriously difficult (J. Turnbull, "CEM's - Sample Handling and Calibration", In proceedings for CEM98, International Conference on Emission Monitoring, Teddington, UK, April 22.-24., 1998, p. 189). Generation of controlled concentrations of water is particularly difficult, when controlled humidification of a

gas containing reactive or water soluble components have to be performed (US 4,385,910).

However, attempts have been made to generate gas samples  
5 having a known water vapor content in order to establish the amount of loss in a dry analysis system or to establish suitable correction factors for specific analyzers based on a wet measurement principle.

10 One approach has been to pass a dry gas of a known composition through a conventional water bubbler. In a first method a nonreactive carrier gas such as nitrogen or argon is saturated by passing through one or more bubbler stages and then combined with the test gas. In a second  
15 method a dry gas containing the reactive or water soluble specie in a known composition is passed through the water bubbler. In both methods the bubbler temperature, bubbler pressure, number of stages or the water level, and the gas flow rate are varied to produce a desired saturation level  
20 in the gas. Alternatively, the water bubbler may contain a cooler downstream from the bubbler to ensure saturation, and the degree of saturation is then controlled by the cooler temperature and pressure. Both water bubbler methods have major drawbacks. Firstly, the accuracy of the water  
25 addition is dependent of the accuracy of the measurements of temperature and pressure. Subsequent heating to a temperature sufficiently higher than the dew point temperature of the humidified gas is required to avoid downstream condensation. This may introduce problems for  
30 establishing the actual equilibrium temperature. Secondly, the first method while being effective in preventing loss of the reactive or water soluble specie in the humidification trail, has a disadvantage of a limited saturation level in that only a portion of the gas passes  
35 through the bubbler stages. The second method may lead to an additional loss or conversion of the reactive or water soluble specie. Combination of the two methods may be

applied such as enclosed in US (US 4,385,910). By this method it is possible to establish suitable correction factors using the calibration procedures and apparatus enclosed therein. The apparatus is, however, rather  
5 complicated and voluminous, and leads to increased consumption of calibration gas. The method results in an indirect measurement and reduced accuracy unless a continuous and reliable measurement of the water concentration is performed. Further, the method is expected  
10 to require increased service time and are not suitable for automated calibration procedures.

Similar problems as described above, exists for test gas supply systems for laboratory test facilities.

15

It is an objective of the present invention to provide an improved method for dynamic production of gases with a controlled content of one or more gaseous species in a wide range of concentrations. It is a further objective of the  
20 present invention that this improved method is suitable for integration in conventional gas measuring systems and can be used in combination with automated calibration procedures with a minimum of maintenance. It is a still further objective of the present invention that the method is  
25 applicable for a wide range of gaseous species, such as gaseous species that are too reactive to be stored in gas cylinders at known, stable concentrations for extended periods (e.g. ammonia, hydrogen chloride, chlorine, nitrogen dioxide etc.) or gaseous components which are not  
30 available on pressurized gas cylinders such as mercury.

#### BRIEF DESCRIPTION OF THE INVENTION

In a broad aspect the invention relates to a method for producing a gas having a controlled content of one or more  
35 species. The controlled content could be the content of water in a gas used for e.g. calibration purposes. The content of the species is regulated by mass transfer of one



or more substances between a first fluid and a current of a second fluid. In a preferred aspect of the invention, the second fluid is in a gas phase.

- 5 In the broad aspect, the method comprises contacting the first fluid with at least a part of the outer surface of a hollow tubular member at least a part of which comprises a semipermeable membrane and contacting the second fluid with at least a part of the inner surface of said tubular  
10 member.

According to the invention the mass transfer of species between the first and the second fluid is governed by a concentration gradient - or equivalent a partial pressure  
15 gradient - between the first and the second fluid. The species added to or subtracted from the second fluid are the one or the ones which should be added to or subtracted from the second fluid in order to produce the desired gas.

- 20 Even though the mass transfer in many of the preferred embodiments of the invention takes place from the first to the second fluid in order to produce the desired gas, the method can also be used to remove unwanted species in a gas and thereby producing a gas without the unwanted species.  
25 In such a case the mass transfer is similarly governed by a partial pressure (or concentration) gradient existing between the first and the second fluid.

After the second fluid has been in contact with the outer  
30 surface of the hollow tubular member and thereby has been in contact with the semipermeable membrane, the second fluid is guided to an outlet plenum.

- In this plenum the temperature and the pressure of the  
35 second fluid is measured. This measurement can be performed periodically, randomly or constantly depending of the

purpose of producing the gas having a controlled content of one or more species.

5 The purpose of measuring the temperature and the pressure is that the concentration of the transferred species in the second fluid is mathematically derivable from the temperature and the pressure.

10 If the content of the transferred species in the second fluid is not the one aimed at in the outlet plenum, the rate of mass transfer may be altered by adjusting heat added or subtracted to the first and/or second fluid, whereby the temperature in the outlet plenum is adjusted.

15 Therefore, if a gas is to be produced having a very precise amount of a specific species the temperature must be measured more often than if only a fluid which is prescribed to have only an approximate amount of specific species is to be produced.

20

In the first case the produced gas could be a gas used for calibration purposes and in the latter case the gas could be air which should be humidified for air conditioning purposes.

25

The location of where heat is added to or subtracted from the first and the second fluid depends more on an actual design of an apparatus for carrying out the method according to the invention than on the nature of the method  
30 according to the invention.

In one embodiment of the invention heat is added or subtracted before the first and the second fluid are contacted with the surfaces of said tubular member. Even  
35 though adding/subtracting heat in the above mentioned manner is an excellent choice, it is preferred that heat is

added or subtracted while the first and the second fluid are contacted with the surfaces of said tubular member.

It should be quite clear that a combination of the two  
5 above mentioned ways of adding/subtracting heat could be combined into an embodiment of the invention where heat is added or subtracted before the first and the second fluid are contacted with the hollow tubular member and while the first and the second fluid are in contact with the surfaces  
10 of said tubular member.

In another and preferred embodiment of the invention the first fluid contacts at least parts of the outer surface of a plurality of hollow tubular members, at least a parts of  
15 each tubular member comprises a semipermeable membrane.

In this preferred embodiment a very little pressure drop exist over the plurality of the hollow tubular member when the second fluid passes through. Furthermore, when a  
20 plurality of hollow tubular members are used an apparatus for carrying out the method according to the invention can be made very compact. In such a case it is preferred that the tubular members are arranged parallel to each other or at angles to each other, thereby defining a membrane array.  
25 This membrane array may be potted into a common housing in order to seal the inner surface from the outer membrane surface

In order for the second fluid to flow through the hollow  
30 tubular members the housing is provided with connections for inlet and outlet flow of the second fluid. The assembly of at least the above mentioned element constitute a module.

35 In yet another preferred embodiment of the method according to the invention the temperature at the outlet plenum is controlled by substantially locating the module within a

thermostatically controlled oven thereby providing a compact unit for producing the gas.

Such a thermostatically controlled oven could be any type of oven wherein the temperature can be controlled. Of course, the precision of controlling of the temperature and the time of response for temperature adjustment for the oven depends similar to the criteria for how often the measurement of the temperature and pressure should take place, on the desired quality of the produced gas.

The common housing may further comprise a manifold for addition of said first fluid to a liquid reservoir located within the common housing. Preferably no through flow or circulation of the first fluid takes place through the common housing in such an embodiment. In order to be sure that a suitable amount of the first fluid is present in the common housing an external buffer reservoir may be connected to the manifold for addition of said first fluid.

20

The external buffer reservoir can be a container for containing a buffer for substitution of consumption of the first fluid, for instance a day consumption, a month consumption, a year consumption etc. The external buffer can also be provided by a connection to for instance a "normal" water supply such as the supply of drinking water. In both situation the flow of the first fluid through the manifold to the common housing could be controlled by a lever gauge, gauging the level of the first fluid in the common housing.

In another aspect of the invention it is preferred to occasionally also measuring the composition of said first fluid. This is of interest when for instance the first fluid is a multi component mixture and one needs to know to actual concentration of the transferred or other species in

the first fluid, in order to for instance replacing the first fluid, changing the temperature, pressure etc.

In still another aspect of the invention the second fluid  
5 at the outlet plenum is substantially saturated with respect to the composition of the vapour phase in equilibrium with the first fluid. A substantially saturated fluid can be used for calibration purposes.

10 In a preferred embodiment the produced gas is used for calibration of gas analyzers and the membrane assembly may constitutes an integral part of a gas analysis system. In such a case it is generally preferred that the first fluid is in a liquid phase. However, if a dense semipermeable  
15 membrane is utilized the first fluid may also be in a gas phase.

In still another aspect of the invention the method is utilized for producing gas which is applied to a air  
20 conditioning plant.

Even though it is not crucial for the method according to the invention it is preferred that the first fluid being substantially at rest.  
25

In another aspect of the invention an apparatus is provided for producing a gas having a controlled content of one or more species by mass transfer of one or more substances between a first fluid and a current of a second fluid, the  
30 second fluid being in a gas phase. This apparatus comprises a hollow tubular member having an outer surface at least a part of which comprises a semipermeable membrane where at least a part of the outer surface is contacted by the first fluid.

35

The apparatus may further comprises a reservoir for housing the first fluid which is at rest. The reservoir communicates with the outer surface of said tubular member.

5 Similar to description relating to the method according to the invention the apparatus can comprise an outlet plenum to which the second fluid flows after contacting said tubular member, means for measuring the temperature and/or pressure in the outlet plenum and means for measuring the  
10 composition of the first fluid.

#### DETAILED DESCRIPTION OF THE INVENTION

Membrane contactors are emerging technologies for  
15 accomplishment of separation processes like gas absorption, stripping and liquid extraction in a very compact apparatus (E. Cussler, "Hollow Fibre Contactors", In proc. from Nato advanced study institute meeting in separation and purification, p. 1-21, 1993). Two fluid phases are brought  
20 into contact with each other by means of a semipermeable membrane. The membrane serves as a barrier between the two fluid phases. The transport of gaseous species across the membrane are generally diffusion driven by an imposed partial pressure gradient. Theoretical description of the  
25 transport processes occurring in membrane contactors are given in e.g. W. S. Ho et al, "Membrane Handbook", Van Norstrand Reinhold, p. 885 - 912, 1992.

For mass transfer of a volatile component from a liquid  
30 phase to a gas phase, the equilibrium partial pressure of the specific component above the liquid phase or at the liquid-gas interface supported by the membrane will provide the driving force for mass transfer of the component from the liquid phase to the gas phase. A well defined partial  
35 pressure of a volatile component above a liquid phase exists, provided the composition, temperature and pressure are known (Reid et al, "The properties of gases and liquids",

4. ed., p. 241-387, 1987). The equilibrium partial pressures may be predicted from correlations such as the Antoine equation (see example 1), Redlich-Kwong or other suitable correlations for the specific system (Reid et al, "The  
5 properties of gases and liquids", 4. ed., p. 241-387, 1987). Alternatively vapor-liquid equilibrium data may be found in tabulated form in DECHEMA Chemistry Data Series: VLE Data Collection etc. Hence, a well defined equilibrium partial  
10 pressure can be established by measurement of the temperature, pressure and composition of the liquid.

It has been found that membrane contactors are extremely efficient for achieving a gas phase substantially saturated with of one or more volatile substances from a liquid phase  
15 provided the contactor is suitably designed (see below). Further, it has been found that only a part of the semipermeable membrane need to be in contact with the liquid in order to be active for transport - all the membranes will be exposed to the equilibrium composition  
20 above the liquid phase as long as liquid is present within the contactor (see example 1). Hence, the performance of the membrane contactor calibrator is independent of the liquid level and suitable for automated calibration procedures with little maintenance. Further, the membrane  
25 contactor calibrator may be used for a wide range of volatile components in a wide concentration range. The concentration of the volatile component can be controlled by easily adjustable physical parameters such as temperature, pressure and composition of the liquid. This  
30 significantly reduces the consumption of expensive calibration gases. The membrane contactor calibrator may even be used for production of calibration gases, which are not available in gas cylinders such as mercury. Still further the compactness makes it suitable for integration  
35 in conventional gas measuring systems.

Thus, as mentioned above, one aspect of the present invention relates to a method for producing a gas having a controlled content of one or more gaseous species, i.e. the controlled mass transfer of one or more substances from a first fluid to a current of a second fluid, the second fluid being a gas phase. More specifically, the invention relates to a method for controlled mass transfer of one or more gas species from a first fluid to a second fluid in which

- 10 - the first fluid is contacted with the outer surface of a plurality of tubular members, at least part, but preferable all, of the walls of the hollow tubular members comprising a semipermeable membrane, and contacting the second fluid with the inner surface of said hollow tubular members, the hollow tubular members being arranged parallel to each other or at angles to each other, the plurality of hollow tubular members defining a membrane array, said membrane array being potted into a common housing in order to seal the inner surface from the outer membrane surface, the housing comprising connections for inlet and outlet flow of said second fluid and at least one manifold for addition of said first fluid,
  - said membrane array is used in an assembly comprising means for measuring the liquid temperature, liquid pressure and optionally the liquid composition,
  - said assembly further comprising a controllable heat supply.

The second fluid is generally supplied to the gas production assembly from a gas cylinder. The pressure of the gas is controlled by a conventional pressure regulator and the flow rate controlled by a mass flow controller, a critical orifice, a rotameter with a needle valve or other conventional means for gas flow control and measurement. However, a preferred embodiment for automated calibration is flow control using a mass flow controller.



The concentration of the gaseous species transferred to the gas phase is primarily controlled by adjustment of the liquid temperature and suitable selection of liquid composition. Optionally the gas pressure may also be  
5 controlled using a back pressure valve.

In many applications of the present invention the controllable heat supply will comprise an thermostatically controlled oven for the membrane contactor. In such  
10 applications a well defined equilibrium temperature is achieved by extending the outlet connection to the outlet of the oven before the temperature of the produced gas is increased in a heated sample line. Typically, the gas will be heated to a temperature of 10-200°C above the dew point  
15 temperature of the produced gas, such as 100-150°C above the dew point temperature of the produced gas in the heated sample line. A high temperature is specially preferred to reduce adsorption phenomena when calibration gas is supplied to the sample probe.

20

In some applications, the first fluid may be a pure liquid such as water, mercury, etc. In this case the invention is applied in order produce a gas in equilibrium with the gas phase above the liquid and only one substance is  
25 transferred to the gas. The performance of the present invention for such application is illustrated by example 1.

In other applications, the first fluid may comprise a mixture of liquid components such as an binary mixture,  
30 ternary mixture or an aqueous solution of an electrolyte such as ammonia, hydrogen chloride, chlorine, sodium sulfite/bisulfite, sulfuric acid etc. In such applications more than one component is transferred to the gas. In order to have a well defined equilibrium for extended periods in  
35 such applications, it is necessary to install suitable means for measuring the liquid composition or to ensure that the liquid reservoir is large enough to ensure a

substantially unchanged composition of the liquid. Examples of means for measuring the liquid composition are ion selective electrodes for measurement of the concentration of hydrogen chloride in water, the measurement of the conductivity and/or the pH value in a sodium sulfite/bisulfite solution etc. However, other suitable methods for establishing the liquid composition may be applied. Alternatively, a substantially unchanged liquid composition may be achieved using a large liquid reservoir, which may comprise an external reservoir connected to the manifold for refill of the first fluid.

In many applications no circulation of the first fluid will be employed in order to simplify the assembly, reduce the amount of moving parts and thereby minimize the amount of maintenance required. However, industrial applications for controlled addition of one or more substances to a gas phase may exist, where it may be desirable to circulate the first fluid. Examples of such applications may be the production of reactant gases or controlled conditioning of ambient air e.g. for fruit storage. In such applications the membrane assembly may contain both inlet and outlet connections for the first fluid.

The semipermeable membrane may be in the form of a hollow fibre or a flat sheet. The semipermeable membrane may be a hydrophilic or a hydrophobic micro porous membrane, but may also comprise an asymmetric or composite membrane consisting of a thin nonporous top layer on a micro porous support. To prevent penetration using when using hydrophilic membranes, the gas pressure should be higher than the liquid pressure. To ensure that this is fulfilled during shut down, shut off valves are applied on the gas inlet and gas outlet for this application. In a preferred embodiment, the semipermeable membrane constitutes a hydrophobic micro porous membrane with a maximum pore size to prevent liquid penetration.

Suitable membrane materials are generally found between the various classes of polymers, inorganics and ceramics. The following types of polymers are suitable: polyolefins, such as polyethylene, polypropylene, and polymethylpentene; poly (halogenated olefins), such as polytetrafluoroethylene; polyvinylidene difluoride; polyamides, polyimides; polysulfones; polyacrylonitriles; polyesters; and polyphenylene oxides. Polytetrafluoroethylene (PTFE) such as the Goretex membranes available from W. L. Gore Associates are particularly suitable, although other materials such as microporous polypropylene membranes available from many producers may also be used.

15 A plurality of semipermeable membranes are "potted" in a potting material (e.g. epoxy) in both ends in order to seal the inner membrane surface from the outer membrane surface. The potting of fibres can be carried out in any suitable manner and such procedures are well known in the art (e.g. 20 US 3,422,008, US 3,339,341, US 3,442,389, US 3,455,460, US 3,690,465, US 4,207,192, US 5,264,171, EP 0562520 A1), all of which are included herein by reference. In this way an array of hollow tubular members are formed. In this case it is obvious that only part of the outer surface is 25 accessible for the first fluid.

A hollow tubular member employed in the context of the present invention have one of a variety of cross sectional shapes, e.g. square, rectangular, elliptic (oval) or 30 substantially elliptic, super elliptic or substantially super elliptic, or circular or substantially circular, polygonal or substantially polygonal or the cross section may be irregular etc. Preferably, the cross sectional of the elongated chamber is oblong. Hence, the term hollow 35 tubular members comprises hollow fibres and any other tubular bodies having any cross section e.g. hollow tubular chambers, tube ribbons etc.

The cross-section of the individual arrays are preferably substantially identical throughout the chamber array. For other cross sectional shapes than circular the diameter is  
5 estimated by the hydraulic diameter.

In most applications a high saturation relative to the equilibrium with the liquid phase is desirable. A relative saturation above 90 % is often preferred, such as above 95  
10 % and in particular above 98 %. In some applications, however, a relatively low saturation may be preferred. In such cases a small area per standard liter of gas per minnute will be used and controlled generation of gases are still possible according to the present invention.

15 In order to achieve high relative saturations the membrane contactor must be suitable designed, i.e. the membrane assembly is sized to ensure a substantially saturated gas phase in a compact assembly suitable for integration in  
20 conventional gas measuring systems.

The residence time of the second fluid in proximity to the hollow tubular member is defined as the distance between the inlet plenum and outlet plenum divided by the average  
25 velocity. The residence time of the second fluid needed depends on the specific membrane and membrane wall morphology. In many applications the gas residence time will be in the range 0.01 - 10 seconds, such as 0.1 - 3  
seconds.

30 The area per standard liter gas supplied to the membrane assembly per minute will generally be in the range 0.01 - 25 m<sup>2</sup>/(Nl/min) such as 0.05 - 10 m<sup>2</sup>/(Nl/min). An area per standard liter supplied to the membrane assembly in the  
35 range 0.1 - 5 m<sup>2</sup>/(Nl/min) is considered to provide a good compromise between compactness and mass transfer capability for most membranes.

The volumetric packing fraction (volume of tubular members to the volume of housing) of the membrane module is selected to achieve a suitable sized liquid reservoir for 5 to ensure low maintenance. Suitable volumetric packing fractions are in the range 0.1-0.6, such as 0.15-0.4.

As mentioned above, the present invention is often used as an integral part of a gas measuring system. Such system may 10 comprise a multi component analyzer such as a mass spectrometer, a Fourier Transformed InfraRed (FTIR) analyzer, a laser emission monitor or a bank of analyzers for measurement of several gaseous species. Calibration of such analyzers often involves a calibration sequence where 15 several test gases of various compositions are supplied to the analyzers.

In such aspects of the present invention, several membrane contactors each containing a specific first fluid in 20 contact with the outer surface of the plurality of hollow tubular members may be located in a common thermostatically controlled oven or in separate thermostatically controlled ovens. In this way flexibility in the production of test gases both with respect to the concentration levels and the 25 gaseous species transferred to the gas. For ultimate flexibility with respect to the concentrations, the produced gas may be mixed with a second gas in a mixing chamber.

### 30 DESCRIPTION OF THE DRAWINGS

Figure 1 illustrates a suitable assembly for practising the present invention. A membrane contactor module, A is located in a thermostatically controlled oven, B.

A standard membrane contactor comprises an inlet 35 connection, C, and an outlet connection ,D , for contacting the first fluid with the outer surface of the hollow tubular members. In a preferred embodiment according to the

present invention these connections C and D are used as manifolds for adding the first fluid, but is closed during operation. The second fluid is supplied to the inlet connection for the second fluid, E, and passes the membrane contactor in contact with at least part of the inner surface of the hollow tubular members to the outlet connection for the second fluid, F. In many cases the second fluid is supplied from a gas cylinder at the position, G, and the flow rate of the second fluid is controlled by the mass flow controller, H. The composition of the produced gas may be varied by adjusting the temperature set point for the thermostatically controlled oven, B, adjusting pressure by the back pressure valve, I, or the composition of the first fluid. The actual temperature and the pressure of the second fluid at the outlet for the second fluid is measured by the sensors, J, and K. For multi component first fluids such as electrolyte solutions the assembly comprises an additional sensor (not shown) for measurement of the liquid composition. The signals from the sensors I-J may communicate with an external processor (not shown) comprising an algorithm for calculation of the composition of the produced gas. This processor may be a part of a gas analyzer. The produced gas is transferred to a heated sample line, L, mounted on the outer surface of the thermostatically controlled oven, where the gas is heated to a temperature of at least 10°C above the dew point temperature of the produced gas. The connection between the outlet for the second fluid and the heated sample line is preferably made from low heat conducting materials such as PTFE and/or made sufficiently long to ensure that the measured temperature is the evaporation temperature.

Figure 2 shows an assembly similar to figure 1 further comprising an external buffer reservoir, M, connected to

one of the manifolds for adding the first fluid. The external buffer reservoir may be located outside or inside the thermostatically controlled oven.

5 Figure 3 is a schematic drawing of the experimental set up used for testing the performance of a membrane contactor as an equilibrium device for humidification of a dry gas as described in example 1. The heated sample line, L, is connected to a commercially available process mass  
10 spectrometer, M, (Quadropole Gas Analyzer mark I available from FLS miljø a/s). Part of the gas can be withdrawn from the Swagelock T fitting, N, before entering the QGA multicomponent analyzer for parallel discrete gravimetric analysis.

15

Figure 4 shows the variation of the volumetric equilibrium concentration of water vapor as a function of the liquid temperature and pressure.

20 Figure 5 shows experimental data for the relative saturation of the nitrogen phase leaving the membrane contactor as a function of the gas residence time.

Figure 6 shows experimentally determined response times for  
25 a measuring system consisting of a sample probe, a heated sample line, and a QGA mark I multi component gas analyzer for a dry HCl and a wet HCl calibration gas. Both calibration gases had a HCl concentration of approximately 50 ppmv. The wet HCl gas was generated according to the  
30 present invention. Details about the experiment are given in example 2.

Figure 7 illustrates an apparatus for producing a gas having a controlled content of one or more species. The  
35 second fluid is supplied to a module, A, at the inlet plenum for the second fluid at the position B. The second

fluid contacts at least part of the inner surface of a tubular member during the passage of the module.

The module comprises an reservoir, C, for housing the first  
5 fluid being substantially at rest, said reservoir communicates with the outer surface of said tubular member. The module further comprises manifolds, D, for adding said first fluid. The second fluid flows to the outlet plenum, E, which contains means for measuring the temperature, F,  
10 and/or pressure, G. The produced gas having a controlled content of one or more species from the first fluid is withdrawn from the position, H.

Figure 8 illustrates an apparatus for humidifying the dry  
15 gas from an air conditioning unit. The dry gas from the air conditioning unit enters the apparatus at the position A. The gas is splitted into two streams, C and D at the splitting point B. The gas stream C enters the inlet plenum for the second fluid in the membrane module, F, and passes  
20 the module in contact with at least part of a hollow tubular member. The membrane module comprises a reservoir, G, for housing the first fluid being substantially at rest, said reservoir communicates with the outer surface of said tubular member.

25

The second fluid substantially saturated with water and/or other species from said first fluid is remixed with the remaining part of the gas from the air conditioning unit at  
30 the mixing point, H. The flow ratio of the gas streams C and D, is controlled to the desired relative saturation of the produced gas at the position, I, by flow restrictions located in the dashed area E. These flow restrictions is designed to maintain the same pressure drop between the



locations B and H for both streams at the desired flow ratio.

#### EXAMPLES

5

##### EXAMPLE 1

*Membrane contactor as an equilibrium device for humidification of a dry gas.*

A commercially available membrane contactor with  
10 hydrophobic micro porous hollow fibres made from polypropylene (Enka 02P06) was located in a thermostatically controlled oven as shown in figure 3. The hollow fiber membrane contactor contained 400 cm<sup>2</sup> hollow fibers of PP with an inner diameter of 0.6 mm and and outer  
15 diameter of 1.0 mm, a porosity of about 75 % and an average pore size of 0.2  $\mu$ m. The active length of the fibres is about 23 cm. Distilled water was filled into the reservoir for the first fluid on the outer surface of the hollow tubular members through the connections C, D. The  
20 connections were hereafter sealed. The set point of the thermostatically controlled oven was adjusted to 40°C and the liquid was allowed to be heated to oven temperature over night. Dry nitrogen gas was fed to the inlet for the second fluid, E. The nitrogen flow was controlled by the  
25 mass flow controller, H. The temperature of the humidified gas was measured by the thermocouple, J, and the pressure was measured by the sensor, K. The produced gas was transferred to a heated sample line, L, operated with a temperature set point of 170°C. The heated sample line  
30 was mounted at the outer surface of the thermostatically controlled oven, B. PTFE tubing with an inner diameter of 4 mm and an outer diameter of 6 mm and stainless steel Swagelock fittings were used for all gas connections. A 20 cm PTFE tubing was used for the connection from the back  
35 pressure valve, I, to the heated sample line, L to ensure a

well defined equilibrium temperature. The heated sample line, L, were connected to process mass spectrometer (FLS miljø a/s, QGA mark I), M. This analyzer was initially calibrated by withdrawing a gas sample for discrete  
5 gravimetric analysis at the position N.

An excellent prediction of the partial pressure of water vapor above the liquid water are obtained from the Antoine equation (Reid et al, "The properties of gases and liquids",  
10 4. ed., p. 208-218, 1987):

$$P_{H_2O} = \exp (23.238 - 3841/(T-45)) \quad (1)$$

where T is the liquid temperature in K and  $P_{H_2O}$  is the equilibrium pressure of water in Pascal.

15 The concentration of water in the vapor phase is given by:

$$CH_2O = P_{H_2O}/P_{total} * 100 \quad (2)$$

where CH<sub>2</sub>O is volumetric equilibrium concentration of water in percent and  $P_{total}$  is the total pressure above the water phase in Pascal.

20

Figure 4 shows the variation of the volumetric equilibrium concentration of water as a function of the water temperature and the total pressure above the water phase. As seen the volumetric equilibrium concentration of water  
25 can be widely controlled by variation of adjustable physical parameters such as temperature and pressure.

Figure 5 shows experimental data of the relative saturation of nitrogen leaving the membrane contactor as a function of  
30 the gas residence time. The equilibrium concentration of water was calculated by equation 1 and 2. The gas residence time was varied by varying the gas flow rate. The measured temperature at the gas outlet was 40.6°C. As seen from the figure equilibrium is approached at gas residence times  
35 above about 10 to 20 msec. The same experiment was performed with only 10 % of the water volume filled into liquid reservoir. No significant changes from the results

in figure 5 was observed. This shows that all membrane area is active for transport, no matter if the equilibrium is established above the liquid or in the mouth of the gas filled pores.

5

#### EXAMPLE 2

##### *System response time for dry and wet calibration gases*

The response time for an analyzer is typically specified as the time from zero reading to 90 % of the reading at  
10 infinite time,  $t_{90}$ . The response time for a dry HCl calibration gas directly injected into the measuring cell of the process mass spectrometer used in example 1 (QGA mark I available from FLS miljø a/s) is less than 1 second. However, the response time for a typical measuring system  
15 is considerably larger as will become clear in the following. A test measuring system comprising

- 1) a heated sample probe (M & C type SP21H) comprising a ceramic filter for particulate  
20 removal, a calibration port and an outlet sample port.
- 2) a 10 m heated sample line with 1/8" PTFE tubing is connected to the outlet sample port of the  
25 heated sample probe. A set point of 175°C is used for the heated sample line.
- 3) A QGA mark I process mass spectrometer including a heated inlet operated at a temperature set  
30 point of 150°C.

First, a certified dry calibration gas consisting of 50 ppmv $\pm$ 2% is supplied at a flow rate of 1 Nl/min to the calibration port of the heated sample probe. A gas sample  
35 of 0.5 Nl/min is withdrawn from the sample outlet port to the QGA process mass spectrometer for measurement of the

response time. The measured concentration relative to the maximum concentration is shown in figure 6.

A 10,00 % hydrogen chloride solution (Merck Suprapure) was  
5 filled into an assembly according to the present invention.  
The assembly is similar to the one described in example 1  
except the membrane contactor module from Microdyne was  
replaced with a 1.4 m<sup>2</sup> membrane contactor module from  
Hoechst-Celanese (2,5" x 8" Liqui-Cell Extra-Flow Contactor  
10 ). The outlet temperature of the gas was 45,0°C and the  
total pressure measured at the gas outlet was 119130  
Pascal. Equilibrium data for the vapor pressures of HCl and  
water vapor over a 10 % solution of HCl are given with an  
accuracy better than 2 % in table 3-10 and 3-11 in Perry's  
15 Chemical Engineers Handbook, 6. ed, McGraw-Hill, p. 3-64,  
1984. The vapor pressures of water vapor and HCl over such  
solution is according to this table 61,5 and 0,045 mmHg  
corresponding to 8197 and 5.998 Pascal, respectively.  
Hence, equation 2 results in an equilibrium concentrations  
20 of water vapor and HCl of 6,88 vol. % and 50,34 ppmv,  
respectively. The relative concentration vs. time for the  
produced wet calibration gas is also shown in figure 6.

As seen from the figure the response time ( $t_{90}$ ) of the  
25 measuring system is improved with a factor of about 20  
compared to calibration using a dry calibration gas. The  
improvement can be attributed to changes in the adsorption  
equilibria. The behaviour of other reactive gases is  
expected to be similar although the relative response time  
30 may be different. Hence, the use of wet calibration gases  
may significantly reduce the time needed for calibration  
and thereby result in a higher availability.

## CLAIMS

1. A method for producing a gas having a controlled content of one or more species by mass transfer of one or more  
5 substances between a first fluid and a current of a second fluid, the second fluid being in a gas phase said method comprising
- 10     ▪ contacting the first fluid with at least a part of the outer surface of a hollow tubular member at least a part of which comprises a semipermeable membrane
  - 15     ▪ contacting the second fluid with at least a part of the inner surface of said tubular member,
  - 20     ▪ leading the second fluid to an outlet plenum,
  - 20     ▪ occasionally measuring the temperature and pressure of the second fluid at the outlet plenum and if necessary adjusting the temperature by adjusting the heat added or subtracted to the first and/or second fluid.
2. A method according to claim 1, wherein the heat is added  
25 or subtracted before the first and the second fluid are contacted with the surfaces of said tubular member.
3. A method according to claim 1, wherein the heat is added or subtracted while the first and the second fluid are  
30 contacted with the surfaces of said tubular member.
4. A method according to claim 1, wherein the heat is added or subtracted before and while the first and the second fluid are contacted with the surfaces of said tubular  
35 member.

5. A method according to any of the proceeding claims, wherein

- 5 - the first fluid contacts at least parts of the outer surface of a plurality of hollow tubular members at least a parts of each tubular member comprises a semipermeable membrane;
- 10 - the tubular members being arranged parallel to each other or at angles to each other,
  - the plurality of hollow tubular members defining a membrane array, said membrane array being potted into a
  - 15 common housing in order to seal the inner surface from the outer membrane surface, the housing comprising connections for inlet and outlet flow of said second fluid thereby defining a module.
- 20 6. A method according to claim 5, wherein the temperature at the plenum is controlled by substantially locating the module within a thermostatically controlled oven.
- 7. A method according to claim 5 or 6, wherein the common
- 25 housing further comprises a manifold for addition of said first fluid to a liquid reservoir located within the common housing.
- 8. A method according to claim 7, wherein an external
- 30 buffer reservoir is connected to the manifold for addition of said first fluid.
- 9. A method according to any of the proceeding claims, further comprising occasionally measuring the composition of
- 35 said first fluid.

10. A method according to any of the proceeding claims, wherein the second fluid at the plenum is substantially saturated with respect to the composition of the vapour phase in equilibrium with the first fluid.

5

11. A method according to any of the proceeding claims, wherein a residence time of the second fluid is in the range 0.01-10 s, preferably 0.1-3 s.

10 12. A method according to any of the proceeding claims wherein the membrane area per standard liter of second fluid supplied to the module per minute is in the range 0.1-10 m<sup>2</sup>/(Nl/min), such as 0.5 - 5 m<sup>2</sup>/(Nl/min).

15 13. a method according to any of the proceeding claims, wherein the volumetric packing fraction is in the range 0.1 - 0.6 such as 0.15-0.4.

14. A method according to any of the proceeding claims,  
20 wherein said semipermeable membrane is micro porous.

15. A method according to claim 14, wherein said semipermeable membrane is hydrophobic.

25 16. A method according to claim 14, wherein said semipermeable membrane has gas containing pores.

17. A method according to any of the proceeding claims, wherein said first fluid is in a pure liquid phase such as  
30 water, mercury.

18. A method according to any of the claims 1-16, wherein said first fluid is an aqueous solution of hydrochloric acid, sulfuric acid or ammonia.

35

19. A method according to any of the proceeding claims, wherein said semipermeable membrane material is made of a

- polymer selected from polyolefins, such as polyethylene, polypropylene, and polymethylpentene; poly halogenated olefins, such as polytetrafluoroethylene; polyvinylidene difluoride; polyamides, polyimides; polysulfones;
- 5 polyacrylonitriles; polyesters; and polyphenylene oxides.
20. A method according to claim 19, wherein said semipermeable membrane material is a poly halogenated olefin such as polytetrafluoroethylene.
- 10 21. A method according to any of the proceeding claims, wherein the produced gas is used for calibration of gas analyzers.
22. A method according to any of the proceeding claims,
- 15 wherein the membrane assembly constitutes an integral part of a gas analysis system.
23. A method according to any of the proceeding claims, wherein the first fluid is in a liquid phase.
- 20
24. A method according to claims 1-22, wherein the first fluid is in a gas phase.
25. A method according to any of the proceeding claims,
- 25 wherein the produced gas is applied to a air conditioning plant.
26. A method according to any of the proceeding claims, wherein the first fluid being substantially at rest.
- 30
27. A method according to any of the proceeding claims, wherein the mass transfer takes place from the first fluid to the second fluid.
- 35 28. An apparatus for producing a gas having a controlled content of one or more species by mass transfer of one or more substances between a first fluid and a current of a



second fluid, the second fluid being in a gas phase said apparatus comprising

- a hollow tubular member having an outer surface at  
5 least a part of which comprises a semipermeable membrane;  
at least a part of the outer surface being contacted by the  
first fluid,

- a reservoir for housing the first fluid being  
10 substantially at rest, said reservoir communicates with the  
outer surface of said tubular member.

29. An apparatus according to claim 28, further comprising

15 - an outlet plenum to which the second fluid flows  
after contacting said tubular member and

- means for measuring the temperature and pressure in  
the outlet plenum.

20

30. An apparatus according to claim 29, further comprising

- means for measuring the composition of the first  
fluid.

25

31. An apparatus according to claims 28-30, wherein the  
mass transfer takes place from the first fluid to the second  
fluid.

30

1/8

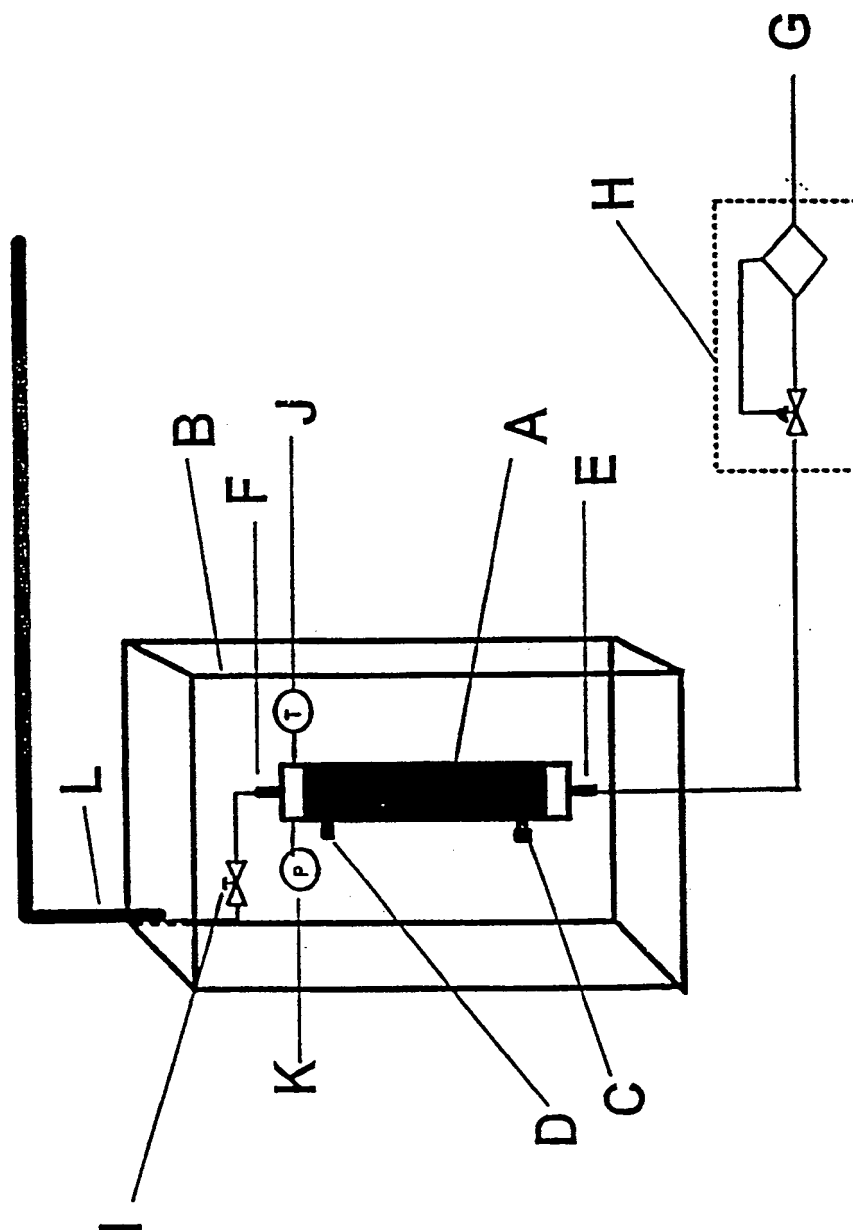


Fig. 1

2/8

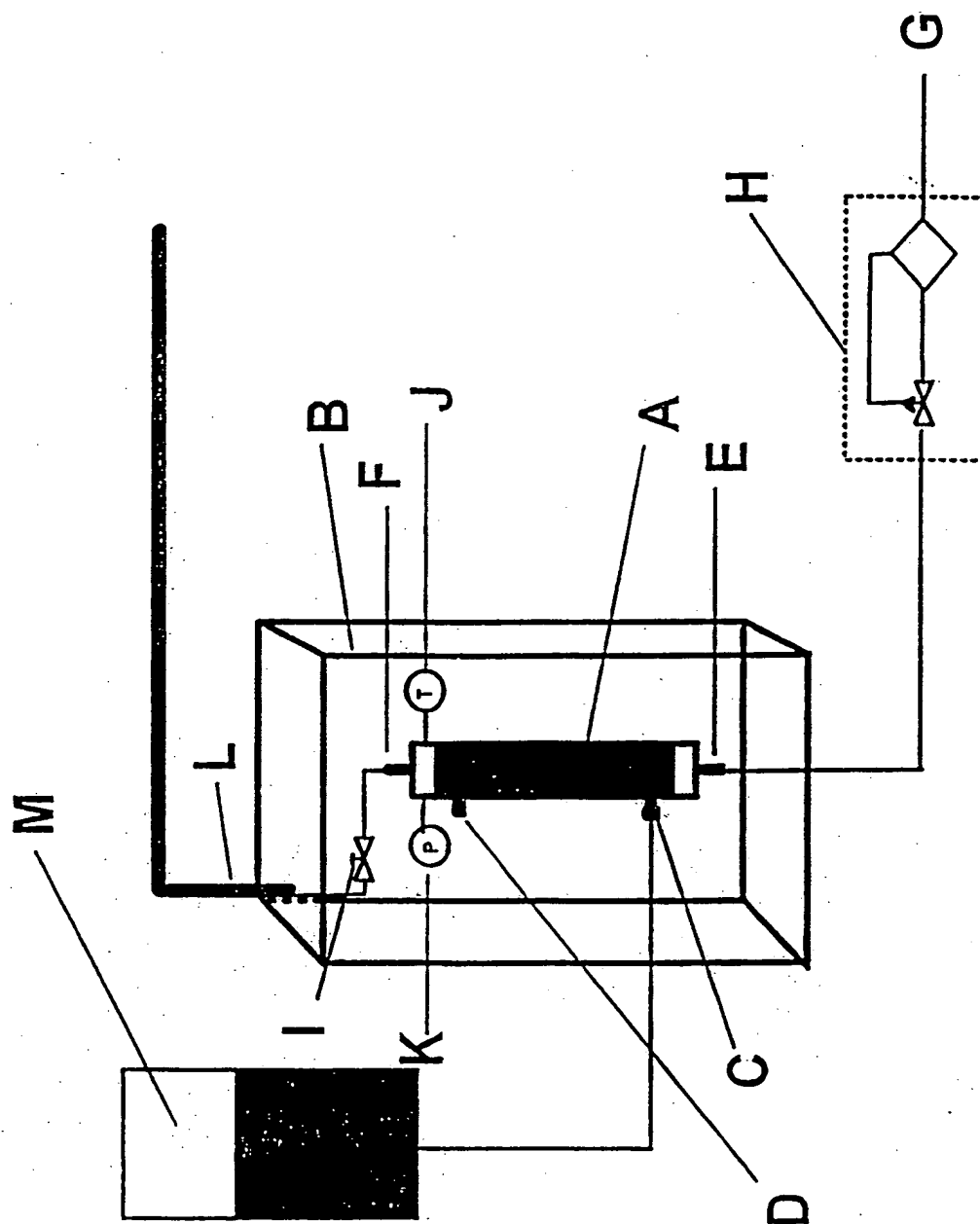


Fig. 2

3/8

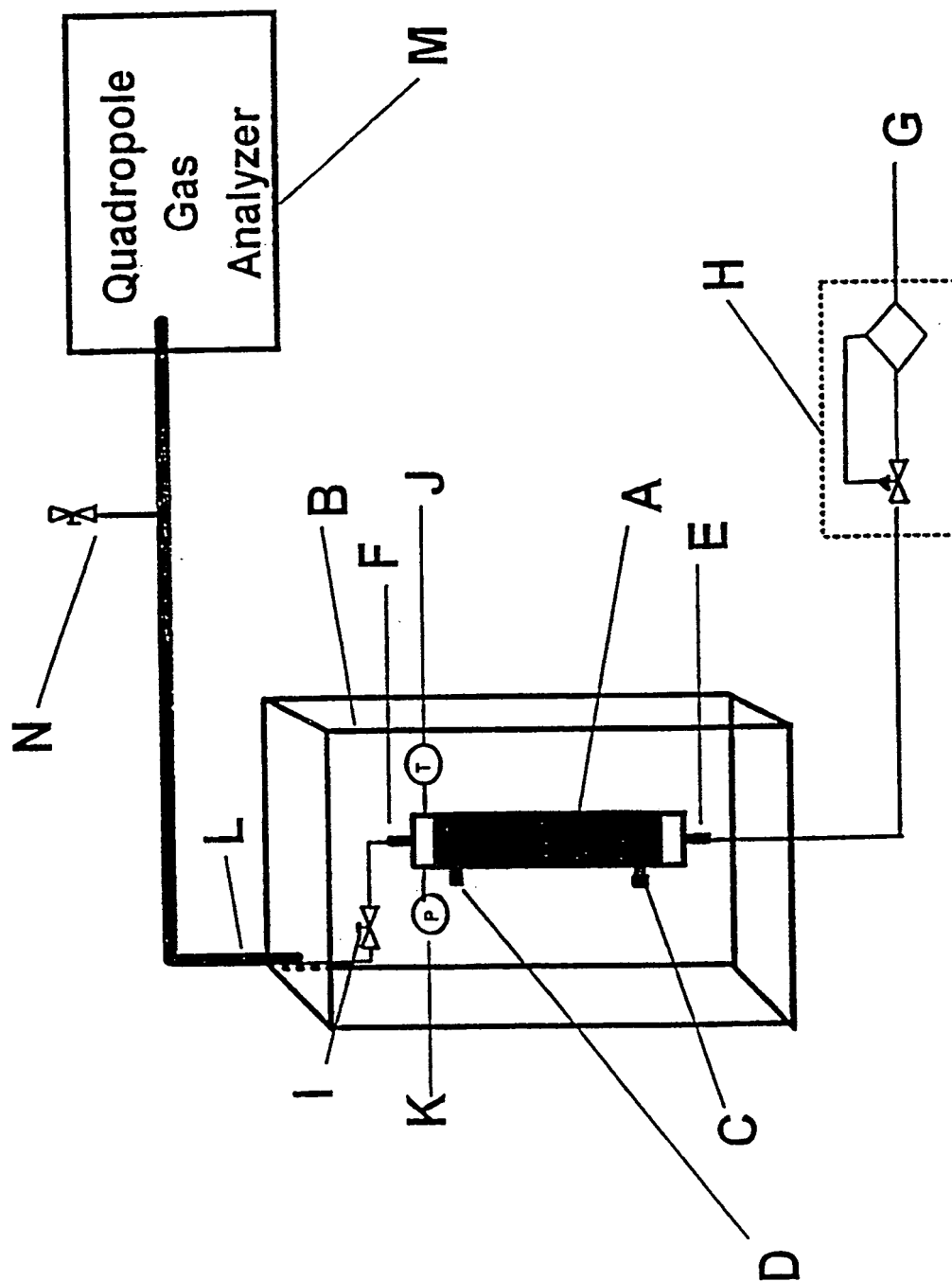


Fig. 3

4/8

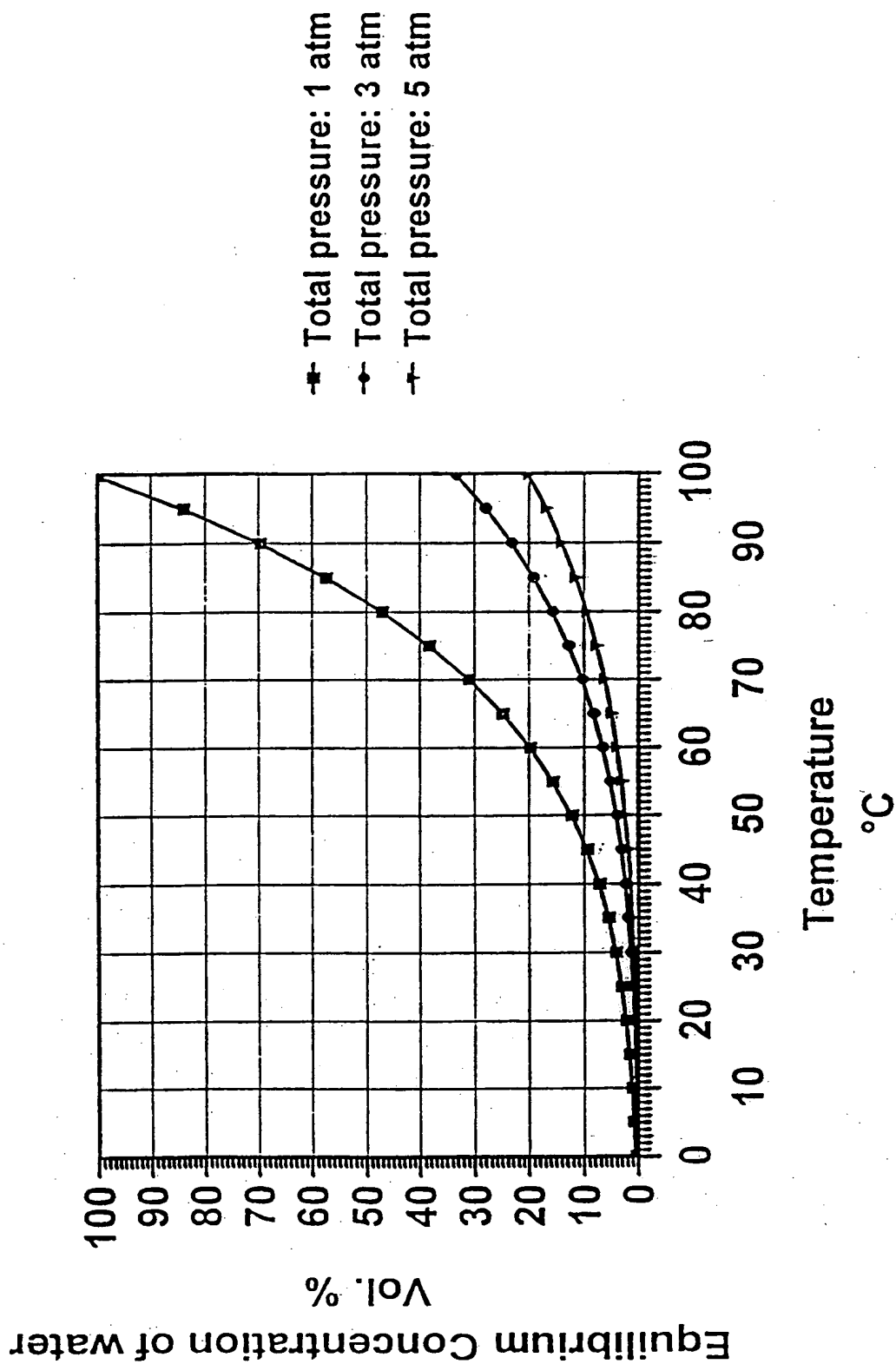


Fig. 4

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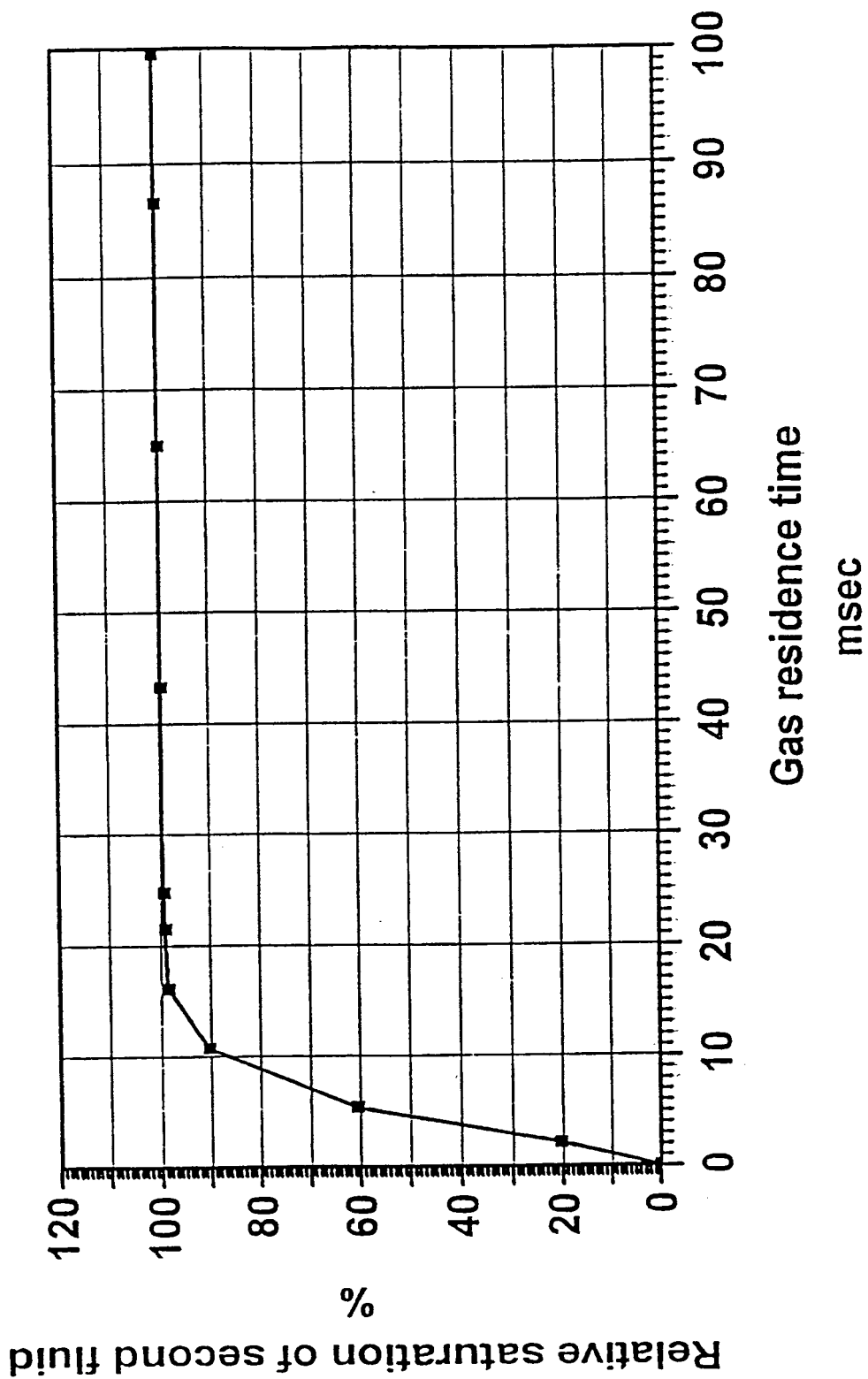


Fig. 5

6/8

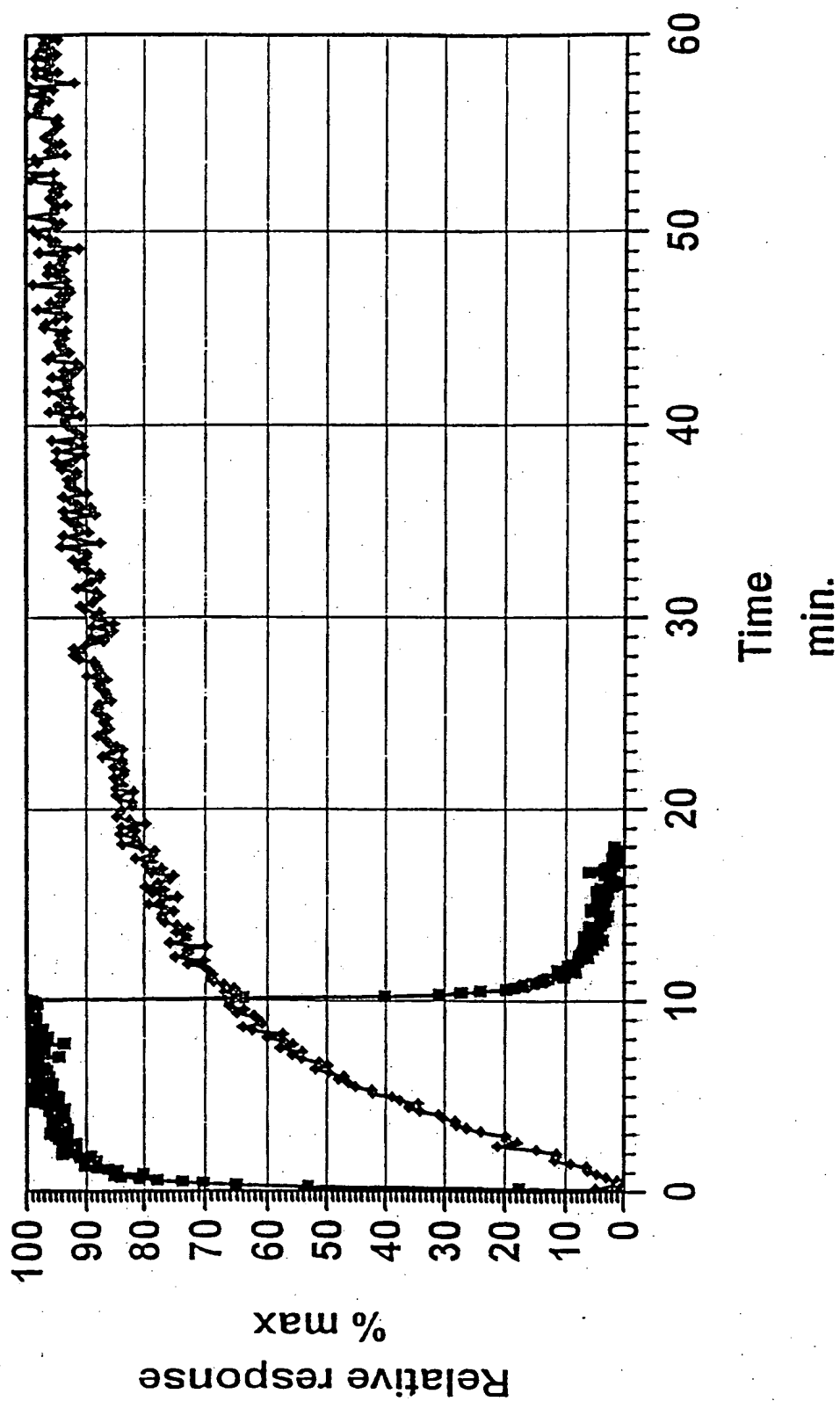


Fig. 6

7/8

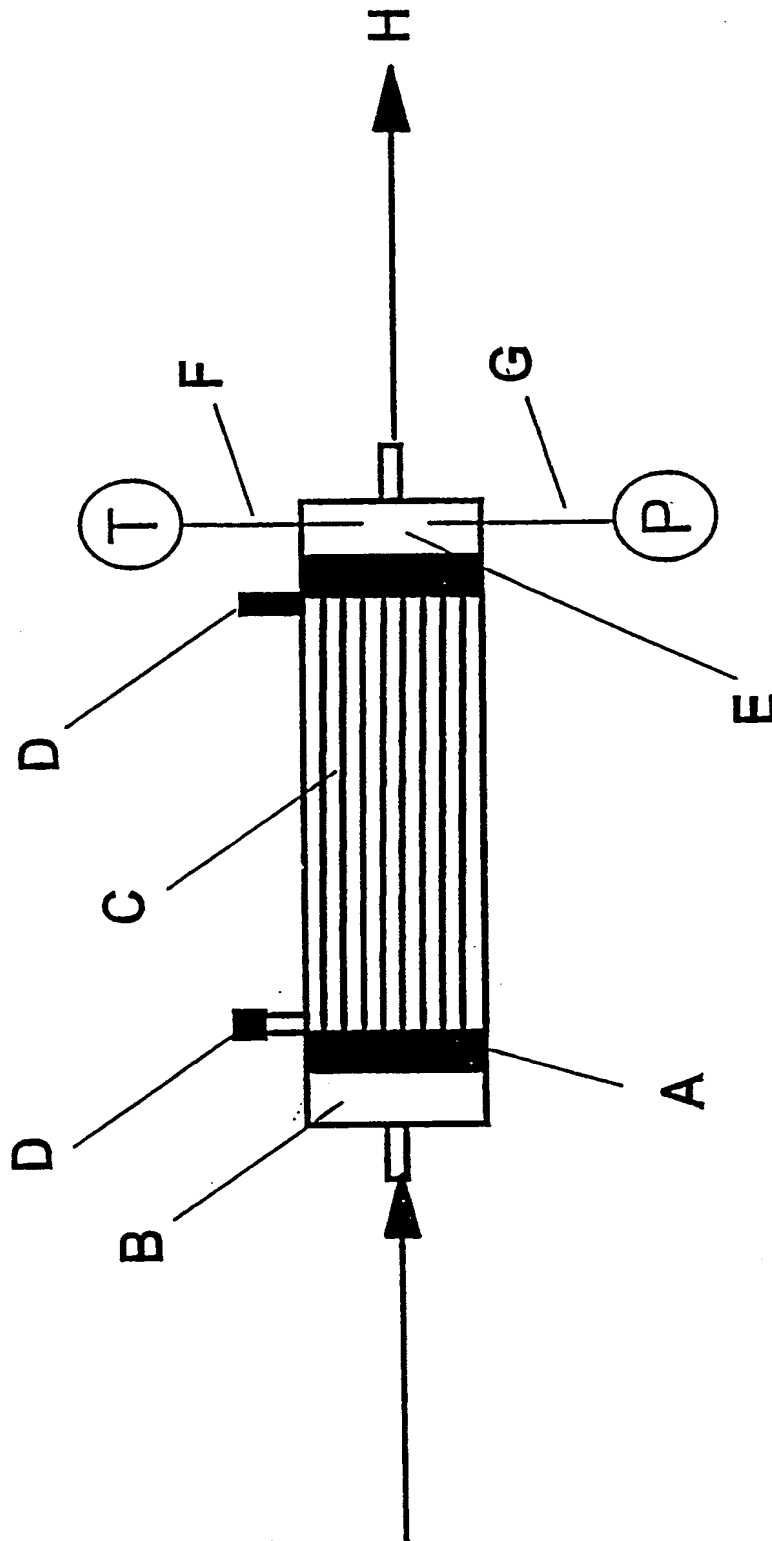


Fig. 7



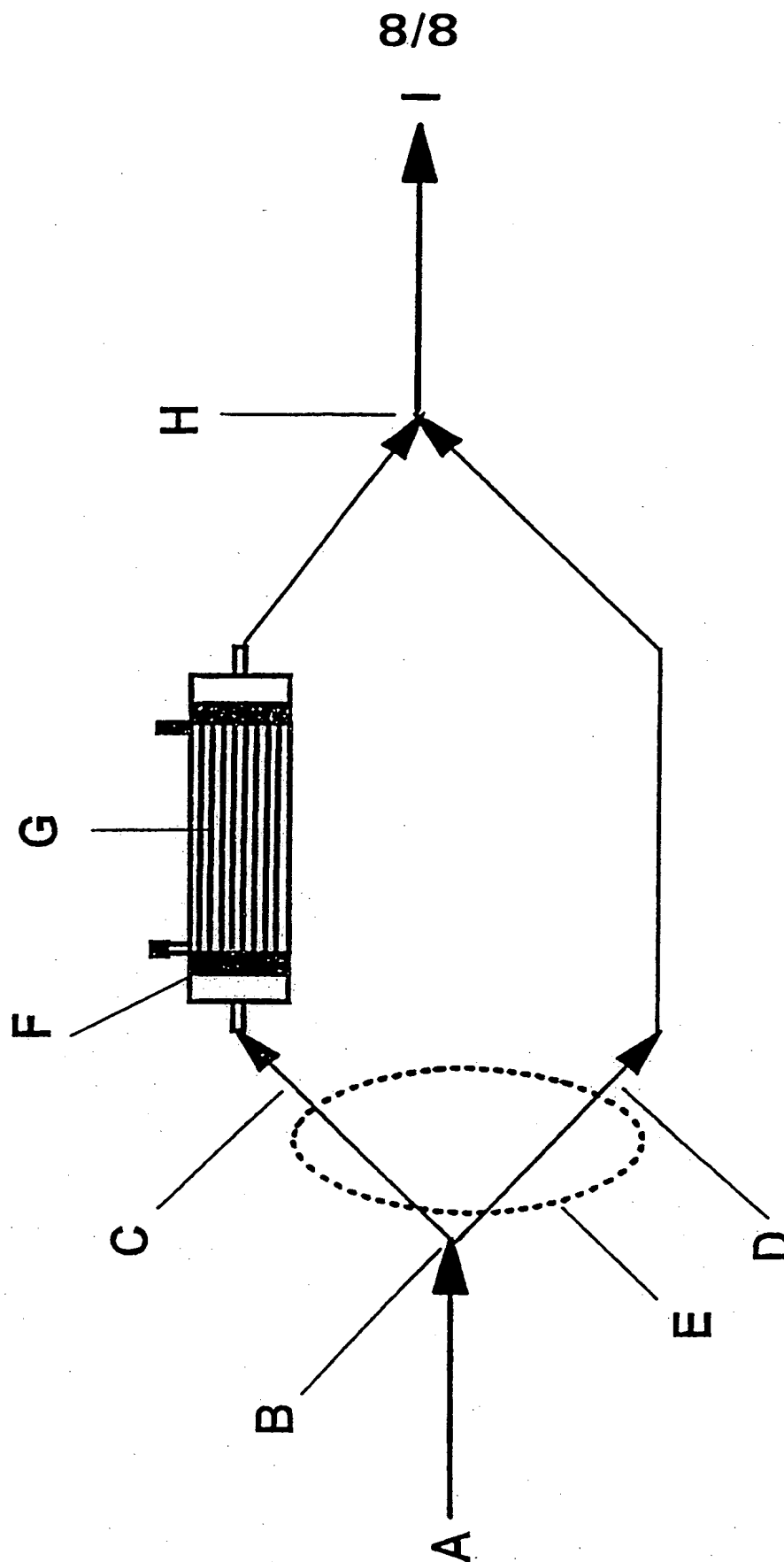


Fig. 8

# INTERNATIONAL SEARCH REPORT

International Application No

PCT/DK 99/00479

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 G01N33/00

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 G01N

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

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Y	the whole document	5,10, 14-24
A		4,6-9, 11-13, 25,29,30
Y	WO 95 35153 A (FLS MILJOE A S ;IVERSEN STEEN BRUMMERSTEDT (DK); BHATIA VINAY KUMA) 28 December 1995 (1995-12-28) the whole document	5,10, 14-24
	-/-	

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

24 November 1999

Date of mailing of the international search report

02/12/1999

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# INTERNATIONAL SEARCH REPORT

International Application No

PCT/DK 99/00479

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

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